A block recursion method with complex wave vectors

LETTER TO THE EDITOR

A block recursion method with complex wave vectors

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Abstract. A new block recursion method using complex wave vectors is developed to calculate the s–p and p–d elements of the inter-site Green functions. A numerical example shows satisfactory results compared with those obtained in conventional band calculations.

It is well known that the recursion method is a powerful tool in calculating the electronic structures of metals, compounds, etc, especially those of complex materials. The recursion method originally developed by Haydock *et al* (1975) has been extended to the form of the block tridiagonalization of the Hamiltonian (Jones and Lewis 1984, Inoue and Ohta 1987, Paxton 1988, Godin and Haydock 1991). The block recursion method has been proved to have the advantage that it preserves the rotational invariability of the Green function expressed in a continued fraction (Inoue and Ohta 1987, referred to as IO hereafter). For example, the inter-site Green function $\mathbf{G}_{ij}$ is expressed by a matrix, the size of which is determined by the number of orbitals on atomic sites, and which is rotationally invariant even if the level of the continued fraction is low. The block-recursion method for the tight-binding d-band model was applied, e.g., to simulate the local stress distributions in transition-metal alloys (Ohta 1989) and to calculate the non-local susceptibilities of intermetallic compounds (Inoue 1992).

The inter-site Green function in the tight-binding d-band model is calculated by using the following formula:

$$\mathbf{G}_{ij} = \langle i|(z - \mathbf{H})^{-1}|j\rangle = \tfrac{1}{2}(\mathbf{G}_{i+j,i+j} - \mathbf{G}_{i-j,i-j}) \tag{1}$$

where $z = E + \mathrm{i}\delta$, $\mathbf{H}$ is the Hamiltonian and $|i\rangle$ and $|j\rangle$ are basis vectors at sites i and j, respectively. Here, the basis vectors are block vectors of size m (number of orbitals on the atomic sites) and $\mathbf{G}_{ij}$ etc are $m \times m$ matrices. It has been pointed out by IO, however, that (1) is useless to calculate the s–p and p–d elements of $\mathbf{G}_{ij}$; in other words, these matrix elements are identically zero since $H_{ij}^{\mu\nu} = -H_{ji}^{\mu\nu}$ for s–p and p–d elements. (Note that $H_{ij}^{\mu\nu} = H_{ij}^{\nu\mu}$ as H is a real Hermitian matrix.) In this letter, we present a method to calculate the s–p and p–d elements of the inter-site Green functions in the block-recursion method and show a numerical example.

We first define complex starting vectors:

$$|\pm\rangle = (|i\rangle \pm \mathrm{i}|j\rangle)/\sqrt{2}. \tag{2}$$

Because $\mathbf{G}_{+,+} - \mathbf{G}_{-,-} = \mathrm{i}(\mathbf{G}_{ij} - \mathbf{G}_{ji}) = 2\mathrm{i}\mathbf{G}_{ij}$ for s–p and p–d elements, we have

$$\mathbf{G}_{ij} = (\mathbf{G}_{+,+} - \mathbf{G}_{-,-})/2\mathrm{i} \tag{3}$$

for these matrix elements. All matrix elements apart from the s–p and p–d elements identically vanish in this expression. The recurrence relation is the same as that given before by IO,

$$W_{n+1} B_n^+ = H W_n - W_n A_n - W_n B_{n-1} \tag{4}$$

except that the block vectors W_n are complex. Here $^+$ denotes adjoint and A_n and B_n are block-recursion coefficients. It is clear that A_n is Hermitian. Because $B_n B_n^+$ is given by an inner product of the right-hand side of (4) and hence is Hermitian, $B_n B_n^+$ can be transformed to a positive definite matrix by a unitary transformation. Then we can also make B_n a Hermitian matrix. This procedure is the same as that used previously by IO. Thus, all of the matrix elements of the inter-site Green functions can be calculated by using both (1) and (3).

As for the termination of the continued fraction, we simply approximate $A_\infty = a_\infty I$ and $B_\infty = b_\infty I$, where I is the unit matrix and a_∞ and b_∞ are real constants independent of the orbitals. Although there may be several ways to determine the values of a_∞ and b_∞ from the calculated data of A_n and B_n, here we simply use the same values of a_∞ and b_∞ as determined in the calculation of the on-site Green function because this choice of a_∞ and b_∞ preserves consistency for the band edges. When the symmetry of the system is low, the simple approximation to A_∞ and B_∞ above may produce the undesirable results that the s–s, s–d, p–p, and d–d elements of G_{ij} do not vanish completely. Because these matrix elements of the Green function expanded in terms of moments vanish correctly, we can attribute these undesirable results to the approximate procedure of the termination of the continued fraction. The magnitude of the non-vanishing elements, however, can be small enough when the level of the continued fraction is sufficiently large.

As a numerical example, we calculate non-local susceptibilities of paramagnetic transition metals using the tight-binding model including s, p, and d orbitals. The non-local susceptibility χ_{ij} is given by (Terakura *et al* 1982, Inoue 1992)

$$\chi_{ij} = (2\mu_B^2/\pi) \int_{-\infty}^{E_F} \operatorname{Im} \operatorname{Tr} G_{ij} G_{ji} \, dE \tag{5}$$

where μ_B is the Bohr magneton and Tr is taken over the orbitals. The hopping parameters are taken from data calculated by Papaconstantopoulos (1986) for FCC Ni. The parameters up to the second-nearest neighbours are included. The overlap integrals are neglected. An FCC cluster of 4000 atoms is prepared and A_n and B_n are calculated up to $n = 7$. In these calculations, the Green functions obtained by using the approximate termination of the continued fractions give the desired properties.

The total density of states calculated is shown in figure 1(*a*). The number of recursion coefficients calculated is not sufficient to produce fine structures of the density of states. The qualitative feature, however, is properly reproduced. The calculated results for χ_{ij} are shown in figure 1(*b*) as functions of the Fermi energy E_F for $i = (0, 0, 0)$ and $j = (1, 1, 0)$, (2,0,0), and (2,2,0), which are denoted by χ_{01}, χ_{02}, and χ_{03}, respectively. The result of χ_{01} is consistent with that calculated for Ni metal (Terakura *et al* 1982) in the conventional band calculation. χ_{02} and χ_{03} show an oscillatory change with E_F, which is qualitatively the same as those calculated by Terakura *et al* (1982). A better agreement for χ_{02} and χ_{03} may be obtained by including a larger number of recursion coefficients.

In conclusion, we have presented a method to calculate the s–p and p–d elements of the inter-site Green functions, introducing a block-recursion method with complex wave
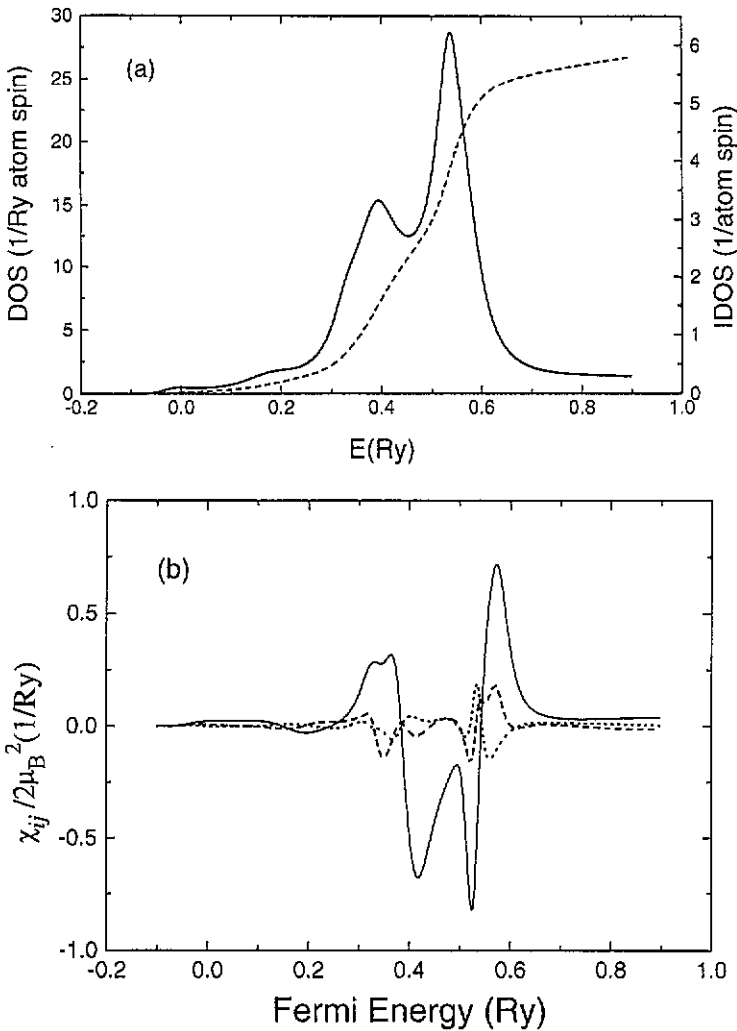
Figure 1. Calculated results for (a) the density of states (full curve) and integrated density of states (broken curve) and (b) the non-local susceptibilities $\chi_{ij}/2\mu_B^2$ for $i - j = (1, 1, 0)$: χ_{01} (full curve), $(2, 0, 0)$: χ_{02} (broken curve), and $(2, 2, 0)$: χ_{03} (dotted curve).

vectors. The numerical example has shown its usefulness. This method will be a powerful tool for studying the electronic structures, electron transfer, etc, in complex materials, e.g., polymers, where s and p orbitals play important roles. In these cases, the overlap integrals must be properly taken into account. Such generalization is in progress.

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